UCRL-JC-123442 Abs

Title:
Unraveling the Kinetics of Petroleum Destruction by Using 1,2-l3C2 Isotopically Labeled Dopants

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Keywords:
Labeling, C-13
Kinetics
Petroleum
Mass Spectrometer, Gas Chromatograph-

Presentation Session Preferences:
First Choice Type: Poster
First Choice Session: Polymers, Surfactants, Petrochemicals
Second Choice Session: Organic Analysis

Abstract:

The stability of crude oil in the subsurface is of continuing interest as the search for new supplies pushes new frontiers. Beyond mere stability, some investigators are developing kinetic models that would predict oil composition as well as occurrence. Two problems arise when deriving these compositional models: (1) it is difficult to unravel the reactions that simultaneously create and destroy a particular component in a complex mixture, and (2) the reactions of a given component by itself are not necessarily the same as in a complex matrix. A new isotopic method involving a double-l3C label detected by gas chromatography mass spectrometry (GC-MS) is presented here for unraveling these reactions. The method is demonstrated by measuring the intrinsic destruction kinetics of labeled n-hexadecane in ordinary n-hexadecane and in three crude oils of substantially different composition: a typical North Sea oil, a high-paraffin oil, and a high-sulfur oil. The unexpected conclusion is that the kinetics of hexadecane destruction are nearly equal in these three dissimilar oil matrices but only 60% as fast as in neat hexadecane.

The use of isotopic labels in kinetic studies is common, but investigations of skeletal reactions usually use a single labeled atom. A double-l3C isotopic label is much easier to follow in an oil matrix by conventional GC-MS. The natural abundance of l3C is 0.011, so the normal probability of finding two l3C atoms in a small mass spectrometric fragment is very small: O.00012 for an ethyl radical (m/z = 31) and 0.00036 for a propyl radical (m/z = 45). This low natural abundance makes it possible to follow both the disappearance and the appearance of doubly labeled species at very low dopant levels. A 1 wt % dopant of 1,2-13C2-n-hexadecane is easily detected in a m/z = 31 mass chromatogram with a signal-to-noise ratio of several hundred. Even though the added 13C is only 10% of the total 13C in the oil, it represents 99% of all mass 31 ethyl groups in the oil.

This paper will report on this new method, along with the results of heating several oils in sealed capillary tubes at temperatures from 310 to 360 °C, from times ranging from a few days to over a year, and using a variety of multiple-13C labeled compounds.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.